

XIII. *Farther Experiments relating to the Decomposition of dephlogisticated and inflammable Air.* By Joseph Priestley,
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Read April 7, 1791.

THE doctrine of *phlogiston*, and that of the *decomposition of water*, have long engaged the attention of philosophical chemists, and experiments have sometimes seemed to favour one conclusion, and sometimes an opposite one. I have myself been very differently inclined at different times, as appears in my publications on the subject; and I am hardly sensible of a wish which way this important controversy, as it may be called, be decided, notwithstanding the part that I have taken in it. I cannot help thinking, however, that the experiments, an account of which I shall now lay before the Society, are decisive in favour of the composition of an acid from dephlogisticated and inflammable air; and, therefore, that the opinion of these two kinds of air necessarily composing *water* cannot be well founded. It is, indeed, sufficiently evident, that the same elements likewise compose *fixed air*, and therefore it is the less extraordinary that they should compose another acid.

The doctrine of phlogiston I would, however, observe, will not be affected by the most decisive proof of the composition of water from dephlogisticated and inflammable air; since this would

would only prove, that phlogiston is one constituent part of water; which is an opinion that I have advanced, and mentioned on several occasions; and it is the less extraordinary, as water resembles metals in the remarkable property of being a pretty good conductor of electricity. What I shall now allege, however, will make it very doubtful, whether pure water be ever formed by the union of dephlogisticated and inflammable air; and perhaps make it more probable, that water, as I have lately advanced, is only the *basis* of those kinds of air, as well as of every other kind.

It was objected to my former experiments on the decomposition of dephlogisticated and inflammable air, by firing them together in a copper vessel, which always produced an acid liquor, that this acid came from the *phlogisticated air* with which the dephlogisticated air that I made use of was necessarily more or less diluted; or from that which I could not wholly exclude, as a part of atmospherical air, when I exhausted the copper vessel by means of an air-pump.

To obviate this objection, I then observed, that I not only constantly found that the more phlogisticated air was contained in the two other kinds of air (mixed in the proportion of two measures of inflammable air to one of dephlogisticated) the less acid I got; but that, when I purposely mixed any given quantity of phlogisticated air with them, it appeared not to have been at all affected by the process, but remained the very same, in quantity and quality, as before. Still, however, because Mr. CAVENDISH, though in a very different process, had found nitrous acid to result from the decomposition of phlogisticated and dephlogisticated air; and because M. LAVOISIER and his friends had found nothing but pure water after the slow burning of dephlogisticated and inflammable air; it was maintained

maintained by the favourers of their system, that the *water* only in the liquor which I procured came from the union of the two kinds of air, and the *acid* from the *phlogisticated air* which I had not been able to exclude.

But let any person only consider the very small quantity of nitrous acid which was procured by Mr. CAVENDISH from the certain decomposition of 3194 grain measures of atmospherical air, amounting to more than $6\frac{1}{2}$ ounce measures in one case, and of 2710 grain measures, amounting to $5\frac{1}{2}$ ounce measures in another case (Phil. Trans. Vol. LXXVIII. p. 264. 268.), three-fourths of which was phlogisticated air; and the vastly greater quantity which I procured (Ibid. p. 324.), when it could not be proved, that a particle of phlogisticated air was decomposed, and think whether it was at all probable, that the acid came from this kind of air, and not from the union of the dephlogisticated and inflammable air, which evidently disappeared in very great quantities. This circumstance alone might have satisfied those who interest themselves in this question; but it does not seem to have been attended to.

I have now, however, effectually removed the objection above mentioned, by intirely excluding all phlogisticated air from the process; the dephlogisticated air which I at present use being so pure, that it contains no sensible quantity of phlogisticated air. I also make use of no air-pump, but first fill the copper vessel with water, and then displace it by the mixture of the two kinds of air; yet, in these circumstances, in which all phlogisticated air is excluded, I procure even a stronger acid than before.

The paper that I send along with this article contains the dry residuum of the turbid green liquor, produced by a single explosion of a mixture of two parts inflammable and something

thing more than one part of dephlogisticated air, in a copper vessel which holds thirty-seven ounces of water; and a little more must have remained in the vessel, which I could not get out by draining or shaking it. It is most evident, therefore, that the acid necessary to dissolve so much copper must have come from the union of the dephlogisticated and inflammable air, because there was nothing else in the vessel. The inflammable air was procured from iron by means of steam.

This very pure dephlogisticated air I first imagined could only be got by the process in which I observed (*Experiments on Air*, Vol. II. p. 170.) that I once before procured it, though I then supposed the extraordinary result to be accidental; because in other circumstances I have sometimes had it very pure when I could not succeed in a second attempt of the same kind. It was by heating the yellow product of the solution of mercury in spirit of nitre, without suffering the red precipitate into which it is converted by heat to come into contact with the external air, from which I thought it probable that it might attract some phlogiston. Afterwards, however, I found that this circumstance makes no difference whatever; and that the air so procured *appeared* to be purer, arose from the greater purity of the *nitrous air* which I made use of as a test, and which I got from mercury, and not from copper, the nitrous air from which I find to be much less pure. For trying the dephlogisticated air yielded by some red precipitate which had been prepared many months by the nitrous air from mercury, it appeared to be as pure as that which was procured in the manner above described.

That the dephlogisticated air which I now made use of was sufficiently pure for my purpose, appeared from mixing one measure of it with two of nitrous air, when the whole quantity

tity was reduced to less than four hundredth parts of one measure; so that it is probable that, by a more accurate proportion of the two kinds of air, and greater address in mixing them, they might have almost intirely disappeared. There is besides some reason to think, from the great variety in nitrous air, that the greater part of this very small residuum comes from the nitrous air, and not from the dephlogisticated.

It will be said, how is it possible to reconcile the result of this experiment with that of M. LAVOISIER and his friends? which I was by no means disposed to question after the publication of the *Extract from the Register of the Academy of Sciences for August 28, 1790*, in the seventh volume of the *Annales de Chimie*, in which a distinct account is given of a large quantity of very pure water procured from the slow combustion of the two kinds of air above mentioned: for before this it was acknowledged, that some little acid was always found in the water so procured.

But my late experiments, besides ascertaining the fact of the production of nitrous acid from the decomposition of dephlogisticated and inflammable air, throw some farther light on the subject, and may in some measure explain their result; for I am now able to procure, in my own process, either nitrous acid or pure water, from the same materials.

I constantly observe, that if there be a surplus of dephlogisticated air, the result of the explosion is always the acid liquor; but that if there be a surplus of inflammable air, the result is simply water. That phlogisticated air is not in all cases affected by this process, I completely ascertained, by admitting a little common air into that mixture of the two kinds of air which always produced water, and finding nothing but water in the result.

I find, however, that, agreeably to the experiments of Mr. CAVENDISH, phlogisticated air is decomposed in this process, when there is not enough of inflammable air to saturate the dephlogisticated air; though when there is a redundancy of inflammable air, there is even a production of phlogisticated air. Putting 0.5 oz. m. of phlogisticated air to a mixture of two ounce measures of inflammable air and 1.5 oz. m. of dephlogisticated air, the whole was reduced by explosion to 1.05 oz. m. of the standard of 1.1, with two measures of dephlogisticated air, which appears by computation to contain no more than 0.388 oz. m. of phlogisticated air; so that 0.112 oz. m. had been decomposed in the process. When there is a sufficient quantity of inflammable air, the phlogisticated air always remains unaffected in this process, as appears by mixing any quantity of it with the two kinds of air to be exploded, and finding the very same quantity, as I have repeatedly done, in the residuum.

That when there was a sufficiency of inflammable air for the purpose, phlogisticated air is even *produced* in this process, was evident from my never being able to diminish any quantity of dephlogisticated air by inflammable air so far as by good nitrous air, and the residuum always containing phlogisticated air. Having exploded two measures of inflammable air with one of dephlogisticated air, which by a mixture of two measures of nitrous air was reduced to 0.04, there was a residuum of 0.1, of the standard of 1.3, which appears by computation to contain 0.0767 oz. m. of phlogisticated air.

The reason why, in my former experiments, I always procured more or less acid, must have been that, without any intention, or suspecting that any thing depended upon it, I must have had some surplus of dephlogisticated air. M. LAVOISIER I also perceive to have taken it for granted, as I did, that
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after either of our processes, any surplus of either of the two kinds of air would only have remained unsaturated, and have been found unchanged in the residuum.

I claim no merit whatever in this observation. It was in consequence of accidentally finding pure water in what I then imagined to be the same circumstances in which I had always before found acid, and which surprized me not a little at the time, that I was led to vary the proportions of the two kinds of air, till at length I succeeded in ascertaining the circumstances on which this remarkable difference in the result depends; but I am by no means able to assign any reason for this difference.

In this state of my experiments I concluded, that *nitrous acid*, though consisting of the same elements with pure water, contains a greater proportion of dephlogisticated air; and in the last edition of my *Observations on Air*, Vol. III. p. 543. I observed, that “substances, possessed of very different properties, may be composed of the same elements, in different proportions, and different modes of combination. It cannot therefore be said to be absolutely impossible, but that water may be composed of these elements,” viz. dephlogisticated and inflammable air.

When I first prepared an account of my late experiments for the Royal Society, I entertained this idea; but I now consider it as at least uncertain, because when I mix the two kinds of air in such proportions as to produce *water*, I find in the residuum much more *phlogisticated air* than I do when *acid* is produced, which affords a suspicion that, in this case, *the principle of acidity* goes wholly into the phlogisticated air, which, as my former experiments shew, actually contains it, though it is not easy to ascertain in what proportion.

Having exploded three ounce measures of a mixture of something more than two parts inflammable air, and one of dephlogisticated, and another equal quantity in which the inflammable air bore a less proportion to the dephlogisticated, the former of which I knew would yield water, and the latter acid, I found the residuum of the former to be 0.57 oz. m. not affected by nitrous air, and weakly inflammable; and in order to find how much phlogisticated air it contained, I mixed different proportions of phlogisticated and inflammable air, and concluded, from the manner of firing *them*, and this *residuum*, that it could not consist of less than one-third of phlogisticated air, *viz.* 0.19 oz. m. But the residuum of the mixture which would have produced acid was 0.62 oz. m. of the standard of 1.0, which I find by computation to contain not more than 0.062 oz. m. of phlogisticated air. I repeated this experiment very many times, and never failed to have a similar result; so that it is very possible that the *pure water* we find may be nothing more than the basis of the two kinds of air; and the principle of acidity in the dephlogisticated air, and the phlogiston in the inflammable air, may combine to form a superfluous acid in the one case, and the phlogisticated air in the other.

This supposition is strengthened by finding that whether the produce be acid, or pure water, the two kinds of air unite in nearly the same proportions. But since water has an affinity to almost every substance in nature, and a peculiarly strong one to the acid and alkaline principles, it may be impossible that it should be wholly free from them; and if they be in proper proportions to saturate one another, and in the same quantities, their presence may never appear.

As the reason why, in my former experiments, I always produced an acid liquor, and never pure water, was my using too

too great a proportion of dephlogisticated air; so the reason why M. LAVOISIER and his friends generally produced but little acid, and at last not at all, must have been, that the *slow combustion* which they made use of gave the principle of acidity in the dephlogisticated air, and the phlogiston in the inflammable air, a better opportunity of escaping, and forming the phlogisticated air in their residuum, of which they have not published any satisfactory account *; and it is probable, that the weight of these elements compared with that of the water which forms the basis of the two kinds of air, may be very small. That excellent philosopher M. DE LUC supposes that they have even no weight at all.

M. LAVOISIER himself, I observe, lays particular stress, (p. 262.) on the *slowness* of the combustion, as if he suspected it to be necessary to his result. This circumstance may also account for my want of success in the attempts that I made to repeat his experiment: for whenever I made a stream of inflammable air to burn in a vessel of dephlogisticated air (which I contrived to do by means of a less expensive, but I own a less accurate, apparatus than his) I always got some acid, though less than in my own process; but I made a larger and stronger flame than I imagine M. LAVOISIER chose to produce.

In the course of these experiments, I found, that when the inflammable air I made use of was from turnings of *cast iron*, there was always a considerable quantity of *fixed air* in the residuum, not less than one-tenth of a measure, after the explosion of two

* Since this was written, Mess. FOURCROY, VAUQUELIN, and SEGUIN, have published a very particular account of their experiment; from which it appears, that, after the combustion of the two kinds of air, there was a pretty large residuum of phlogisticated air, more than was contained in the airs before combustion. See *Annales de Chimie*, for April 1791, p. 35.

measures of inflammable air and one of dephlogisticated; whereas there was either no fixed air at all, or the slightest appearance of it imaginable, when I made use of inflammable air from *malleable iron*, extracted either by means of steam or acids.

The principal of these experiments, as well as those in my former Papers on this subject, will be found to confirm the similar ones of Mr. CAVENDISH; but they prove the source of the *acid* in the results not to be what he imagined, *viz.* *phlogisticated air*, but the union of the dephlogisticated and inflammable air; and they also make it at least doubtful, whether these two kinds of air compose *pure water*.

